

PATENT SPECIFICATION

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 (72) Inventor MERCER DUANE GREGORY



(54) COALESCENCE OF WATER AND OLEOPHILIC LIQUID DISPERSIONS

(71) We, CONTINENTAL OIL COMPANY, of 1000 South Pine Street, Ponca City, Oklahoma, United States of America, a corporation of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to separation of the phases of dispersions of liquid petroleum hydrocarbons and water.

Separation of the phases of dispersions of water and liquid petroleum hydrocarbons is of major importance to industry in the prevention of pollution of the environment and in the conservation of natural resources. Exemplary of a few of the applications are the following: in oil fields, waste waters must have hydrocarbons removed therefrom prior to surface release; brine or fresh water injection fluid should have hydrocarbons removed therefrom prior to use in waterflood operations; hydrocarbons should be recovered from brine waste water prior to disposal in underground formations in order to conserve valuable hydrocarbon resources; waste water streams from offshore platforms should have hydrocarbons removed therefrom before disposal. Streams employed in and released from refineries should or must have liquid petroleum hydrocarbons removed therefrom. In heavy industry, removal of oil from waste waters of aluminum rolling mills, the reclamation of cutting oils, and the removal of oil from brine prior to mineral recovery are important applications. Particularly important applications are evident in marine operations wherein oil should be removed from tanker ballast discharge waters; oils should be recovered from bilge pump discharge waters, and oils should be removed from the separated water discharge from oil spill skimming devices. Many other applications are evident to those skilled in the art,

and any process which improves the recovery of liquid petroleum hydrocarbons from dispersions of such hydrocarbons in water is of major importance to industry and the population as a whole in the prevention of environmental pollution and in the conservation of natural resources.

The separation of liquid petroleum hydrocarbons from water wherein the dispersion is of water in the hydrocarbon is also of major importance. In particular, the removal of dispersions of water in fuels is important to prevent icing during cold weather operation.

Many processes have been developed to separate the phases of dispersions of liquid petroleum hydrocarbons and water. However, a major problem still exists and particularly in the removal of low concentrations of hydrocarbons which are dispersed in water. It is believed that this invention constitutes a significant breakthrough in the effective and economical separation of the phases of dispersions of liquid petroleum hydrocarbons and water.

It is an object of the invention is to separate the phases of dispersions of water and liquid petroleum hydrocarbons using coalescence.

This invention relates to separating the phases of a dispersion of an aqueous liquid and a liquid petroleum hydrocarbon which comprises passing the dispersion through a permeable, flexible foam of polyurethane which has been saturated with liquid petroleum hydrocarbon to coalesce the dispersed phase.

According to this invention, there is provided a process for separating the phases of a dispersion comprised of water and a liquid petroleum hydrocarbon wherein the process comprises passing the dispersion without previous coalescence through a coalescing material constituted by a layer of a permeable, flexible foam of polyurethane which has previously been saturated with liquid petroleum hydrocarbon, at a rate of flow sufficiently low to effect a coalescence of the dispersed phase,

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and at a pressure sufficient to substantially maintain the liquid petroleum hydrocarbon of the dispersion in the liquid state, permitting the thus coalesced dispersion to separate into a liquid petroleum hydrocarbon layer and a water layer, and withdrawing the separate layers.

The invention has particular application to the case where the dispersion is a dispersion of a liquid petroleum hydrocarbon in water wherein the liquid petroleum hydrocarbon dispersed phase comprises a trace to one part by weight of liquid petroleum hydrocarbon per 100 parts of water and wherein a flow rate of 50 to 1000 barrels of dispersion per square foot of foam area per day is employed. The liquid petroleum hydrocarbon can be a crude oil wherein the dispersion contains 50 to 350 p.p.m. crude oil and wherein the depth of polyurethane foam layer is 3.5 to 12 inches.

Dispersions comprise of water and a liquid petroleum hydrocarbon which can be separated according to the process of this invention can be either dispersions of liquid petroleum hydrocarbons in water or dispersions of water in such hydrocarbons.

The term liquid petroleum hydrocarbon as employed in this application includes any petroleum hydrocarbon which is a liquid at a temperature at which water or an aqueous metallic salt solution can exist in a liquid phase, and which is substantially insoluble in water or an aqueous salt solution. By substantially insoluble is meant that the solubility is less than 1 part by weight of material per 100 parts by weight of water or aqueous metallic salt solution.

Preferably, the liquid petroleum hydrocarbon is a liquid at a temperature in the range of 0 to 100° C. Examples of liquid petroleum hydrocarbons include natural petroleum products, distillates or fractions thereof, and refined or synthesized products which can be derived from petroleum such as various crude oils, kerosines, petrols, naphthas, recycle oils, fuel oils, benzene, toluene, hexane, bunker oils and lubricating oils. The process of the invention is presently believed to be particularly applicable to removing dispersions of crude oil from production waters.

The water phase of dispersions which are separated according to the process of the invention can be pure water or can be an aqueous solution having a soluble metal salt dissolved therein. Examples of some common metal salts which are dissolved in water to form aqueous liquids or solutions and which are commonly encountered include sodium chloride, sodium bromide, magnesium chloride, calcium chloride and sodium sulfate. Often, such aqueous liquids are derived from natural subterranean brines or from surface waters. There is no limit to the amount of metallic salt which such aqueous solutions contain dissolved therein except the solubility

of the particular metallic salts. Usually such aqueous solutions do not contain over 25 percent by weight of metallic salts.

The permeable, flexible polyurethane foam which is employed according to the process of this invention has a permeability to water sufficient to allow a practical rate of flow therethrough. What constitutes a practical rate of flow is determined by the economics of each particular situation.

The polyurethane foam can be any open-celled polyurethane foam. *Polyurethanes, Chemistry and Technology*, J. H. Saunders and K. C. Frisch, Volumes I and II, Interscience (1963) and (1964), as well as Kirk Othmer, *Encyclopedia of Chemical Technology*, 2nd Edition, Volume 9, p 853—5 (1966), provide description of many suitable materials and means for preparing them. Permeable polyurethane foams having a density of 0.8 to 7.5 pounds per cubic foot are presently particularly preferred. The polyurethane foam can have a preponderance of either ether linkages or ester linkages or a mixture thereof. Presently, polyurethane foam having a preponderance of ether linkages is particularly preferred. Such polyurethane foams are widely available as items of commerce and can be obtained from any of a number of suppliers.

The process of this invention is particularly applicable for coalescing liquid petroleum hydrocarbons from dispersions of liquid petroleum hydrocarbons in water (or brine). Most satisfactory results are often obtained when such dispersions have in the range of a trace to 1 part by weight of liquid petroleum hydrocarbon per 100 parts by weight of water or aqueous solution, but dispersions having more than 1 part per 100 can also be satisfactorily separated. Indeed, the process of the invention is applicable for coalescing a dispersion comprising water and a liquid petroleum hydrocarbon wherein the liquid petroleum hydrocarbon comprises any insoluble portion of the dispersion.

According to this invention, the polyurethane foam through which the dispersion is passed must have become so saturated with liquid petroleum hydrocarbon under the particular flowing conditions employed that coalescence occurs in the process. This critical feature of the present invention is a major factor in distinguishing it from the prior art of which British 1,210,967 and U.S. 3,617,551 are exemplary. Heretofore, it has been disclosed that dispersions of water and oleophilic liquid have been passed through a material such as polyurethane foam, but it has not been disclosed that such foam has ever reached the point of coalescing the oleophilic liquid. Instead, prior to reaching that point, the material such as polyurethane foam has been subjected to a squeezing step to remove the oleophilic liquid. The present invention

provides a tremendous improvement over such prior art methods in that the squeezing step is eliminated with consequent elimination of expensive and break-down prone mechanical contrivances to accomplish that step. A totally new, advantageous, and unexpected result is effected.

According to a presently preferred mode of operation, temperatures of 0—100° C are employed. However, the only requirement with regard to temperature is that both petroleum hydrocarbon and aqueous liquid be in the liquid state. Pressures near atmospheric are preferred because of convenience, though higher or lower pressures can be employed if desired. If gases are dissolved in the hydrocarbon and/or aqueous phase, pressure sufficient to maintain the gases in solution is preferred. A rate of flow of 50 to 1000 barrels of dispersion per square foot of foam layer per day is presently preferred for most satisfactory results. However, higher or lower rates of flow can be employed if desired.

According to one presently particularly preferred mode of operation, the process of the present invention is employed to separate the phases of a dispersion of a liquid petroleum hydrocarbon (eq. crude oil) in water, said dispersion being the aqueous effluent from a conventional API (i.e. American Petroleum Institute) separator, wherein the effluent is polished to a very low level of hydrocarbon in water.

According to one presently preferred mode of operation, a bed of permeable, flexible, polyurethane foam is situated so as to fill a vessel. A dispersion comprising a liquid petroleum hydrocarbon in water (or aqueous solution) is passed upwardly through the bed. Upon saturation of the polyurethane foam, the hydrocarbon dispersed phase is coalesced into droplets which then, if less dense than the aqueous liquid, rise to the top of a liquid reservoir situated above the polyurethane foam bed. Thereupon, the hydrocarbon forms a layer situated above the aqueous layer if the hydrocarbon liquid is less dense than the aqueous layer. Most liquid petroleum hydrocarbons are less dense than water. Portions of the hydrocarbon layer and the aqueous liquid layer are continually drawn off, thus effecting separation.

Though a continuous flow upward through a polyurethane foam constitutes one presently preferred mode of operation, the invention is not so limited. The flow of dispersion can be downward through a foam layer or can be in a horizontal direction. The foam can be employed as a wrapping around a feed pipe for the dispersion, the pipe having orifices throughout the region in contact with the foam whereby the dispersion can enter and pass through the foam.

In one presently preferred configuration, the polyurethane foam is separated at intervals

by retainers such as screens to maintain the integrity of shape of the polyurethane foam layer. The foam layer can also be compressed if desired.

If dissolved gases are present in the hydrocarbon or aqueous liquid, sufficient pressure is preferably maintained on the system to keep such gases in solution. Otherwise, gas breaking through the foam layer has a propensity to cause small liquid hydrocarbon droplets to prematurely break from the layer. Such droplets of small size are less desirable in that separation into an liquid hydrocarbon phase and an aqueous phase is less efficient.

To separate some dispersions, it is often highly desirable to employ a polyurethane foam of 2 or more types in layers.

The following Examples are presented to more clearly and fully disclose the invention, but should not be construed as limiting the invention in any manner.

Example 1.

A dispersion of water in oleophilic liquid was prepared by injecting 50 milliliters of 5 weight percent sodium chloride brine into the intake of a centrifugal pump which was continuously circulating kerosine in a 5-gallon reservoir. A small amount of Tretolite (Trade Mark) F-46 surfactant (available from Petrolite Corporation, St. Louis, Missouri) was added in producing the dispersion to produce a more stable dispersion. Upon completion of formation of the resulting dispersion, it was allowed to settle for 30 minutes. Thereupon, the water content of the water in oleophilic liquid dispersion was determined to be 1000 ppm.

A flexible, open-cell, polyurethane foam having a density of 1.55 pounds per cubic foot and having a high content of ether linkages in the polyurethane polymer (obtained from The Upjohn Company of Torrance, California)** was cut into cylinders 3½ inches in diameter by 2 inches in thickness. The cylinders were packed into an elongated cylinder of Lucite (Trade Mark) plastics having an inside diameter of 3½ inches and a height of 16½ inches to form a foam bed having a depth of 11½ inches. The long axis of the coalescer cylinder was vertical. The foam employed in the bed weighed 59.3 grams. A perforated Lucite plastics disk supported the foam bed above a void space of 5 inches. An inlet was provided at the bottom of the coalescer cylinder and an outlet was provided at the top of the coalescer cylinder with a line leading therefrom to a water trap.

**The polyurethane foam had a compression set maximum of 10%, a tensile strength of 15 lbs/in.² minimum, an elongation of 180% minimum, and a resilience of 40% minimum.

Water-kerosine dispersion prepared as specified was pumped through the foam bed in the coalescer at a rate of about 40 ml per hour. This flow rate gave a residence time of about 30 minutes in the foam bed. The effluent from the coalescer was passed to a water trap and the water concentration in the kerosine downstream therefrom was measured after the foam bed had become saturated with the oleophilic liquid and coalescence had begun.

The dispersion was at a temperature of about 25° C. The water concentration in the effluent downstream of the water trap was monitored over the period of the run wherein 39 liters of dispersion were passed through the coalescer. The water concentration of the effluent ranged from 40 to 100 parts per million. This constituted a reduction of over 90 percent of the water dispersed in the kerosine by passage through the coalescer and the water separator.

This Example demonstrates the process of this invention wherein water is coalesced from a dispersion consisting essentially of water in an oleophilic liquid.

Example 2.

An elongated cylindrical coalescer fabricated of Lucite plastics having an internal diameter of 7.5 inches, having a long axis in a vertical plane, having an inlet at the bot-

tom, having a bed depth of 12 inches of the polyurethane foam of Example 1, having a density of 1.55 pounds per cubic foot, thereabove, having a separation reservoir above the polyurethane foam bed, having an aqueous liquid inlet near the bottom of the separation reservoir, a water outlet in the centre of the reservoir and an oil outlet near the top of the separation reservoir, was set up.

In the South Ponca field of Oklahoma, associated with the production therefrom, is a dispersion of South Ponca crude oil (43° API gravity) in water having a temperature of 90° F and having an oil concentration ranging from about 100—200 parts per million therein.

The oil in water dispersion of the South Ponca field was passed to the coalescer and thence upward through the foam bed. After sufficient of the dispersion had passed through the foam bed to saturate the polyurethane foam with oil coalescence begun. Upward passage of the dispersion was continued to coalesce the oil and separate it from the aqueous phase. The oil was drawn from the top of the separation reservoir, and water was drawn from the center of the separation reservoir situated above the foam bed effecting separation into oil and water components.

The following table presents data for the run wherein the oil was coalesced from the oil in water dispersion.

TABLE I

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Press. Drop Across The Bed Δ P, (psi)	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase	Total Hrs. Operated
229	2.0	116	1.8	1
229	2.0	120	1.8	2 1/2
229	2.0	174	2.0	3 1/2
229	2.0	126	1.5	4 1/2
229	2.0	113	1.2	5
229	2.0	180	1.3	6
229	2.7	*	1.2	6 3/4
229	*	194	1.3	7 3/4
*	*	*	1.1	8 3/4
*	4.0	214	2.4	9 1/4

* Data not taken.

This Example demonstrates the effective coalescence of crude oil from a crude oil in water dispersion according to the process of this invention.

Example 3.

The run of Example 2 was repeated except

that the foam bed employed in Example 2 was replaced with two 2-inch beds of the 1.55 pound per cubic foot polyether-based polyurethane foam of Example 1, which were separated and retained by retainers. The following data were obtained:

TABLE II

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Press. Drop Across The Bed ΔP , (psi)	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase	Total Hrs. Operated
229	2.0	164	11.4	2 1/2
235	2.0	*	11.2	3 1/2
262	2.3	*	7.6	4 1/2
242	2.3	*	4.8	5 1/2
252	2.7	*	4.9	6 1/2
271	2.7	*	4.6	7 1/2
235	2.6	142	5.2	8 1/2
235	3.0	*	5.2	9 1/2
262	2.7	*	5.6	10 1/2
235	2.7	*	5.2	11 1/2
229	2.7	*	7.0	12 1/2

* Data not taken.

This Example again demonstrates coalescence of crude oil from a dispersion comprised of crude oil in water. Though the effluent water is not quite as well purified as in Example 2, very good coalescence and subsequent separation is in fact effected.

Example 4.

The run of Example 2 was repeated except

that the foam bed of Example 2 was replaced with two foam beds which were each 2 inches thick, separated and retained in place by retainers. The foam used in the run of this example was a 7.5 pound per cubic foot polyether-based polyurethane foam obtained from The Upjohn Company. The following data were obtained:

TABLE III

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Press. Drop Across The Bed ΔP , (psi)	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase	Total Hrs. Operated
235	3.4	159	4.0	1 1/2
229	3.7	*	4.9	2 1/2
229	3.8	*	5.6	3 1/2
229	4.2	201.6	13.8	5 1/4
229	4.5	*	2.9	6 1/4
229	4.8	*	2.9	7 1/4

* Data not taken.

5 This Example again demonstrates superior coalescence of crude oil from a crude oil in water dispersion according to the process of this invention. However, in this case, a different density and grade of polyurethane foam were employed.

Example 5.

10 The run of Example 2 was repeated except that the foam bed of Example 2 was replaced

with a foam bed comprising an upper layer which was 2 inches thick of 1.55 pounds per cubic inch polyether-based polyurethane foam and a lower layer of 1.55 pounds per cubic foot polyether-based polyurethane foam which was 2 inches thick originally but compressed by retainers to a thickness of 1.25 inches. The layers of the foam bed were separated and retained in place by retainers. The following results were obtained.

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TABLE IV

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Press. Drop Across The Bed ΔP , (psi)	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase	Total Hrs. Operated
229	2.2	204	7.7	1
229	2.2	*	12.0	1 3/4
229	2.5	*	6.1	2 3/4
229	2.2	*	5.8	3 3/4
229	2.7	134	2.8	4 1/2
229	2.7	*	2.6	5 1/2
235	2.6	*	5.4	6 1/2
229	2.7	*	3.8	7
229	2.7	*	4.9	8
223	2.7	*	3.8	9
253	3.0	134	3.4	10
242	3.3	*	3.2	11
223	3.3	*	11.7	12

* Data not taken.

5 This Example again demonstrates the superior coalescence and separation of crude oil from a crude oil in water dispersion according to the process of this invention. Different conditions of operation are demonstrated.

Example 6.

10 The run of Example 2 was repeated except that the bed of polyurethane foam employed in Example 2 was replaced with a bed 3.5 inches deep of a polyester-based polyurethane foam having a density of 6.0 pounds per

cubic foot.*** Also, the dispersion of petroleum in water employed in Example 2 was replaced with a dispersion comprised of about 100—200 parts per million of Grand Isle crude oil from the CAGC Shore Terminal in Grand Isle, Louisiana, at a temperature of about 75° F in 5 percent NaCl brine. The following data were obtained:

***The polyurethane foam had a maximum compression set of 10%, a minimum tensile strength of 15 lbs/in.², a minimum elongation of 150%, and a minimum resilience of 20%.

TABLE V

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase
~ 70		
	200	66
	200	124
	104	37
	83	28

25 This Example demonstrates coalescence and subsequent separation of another crude oil from a dispersion consisting essentially of crude oil in aqueous liquid. Effectiveness of another type of permeable flexible polyurethane foam having another density is also demonstrated.

Example VII.

The run of Example 6 was repeated except that the bed of polyurethane foam employed therein was replaced with a bed 3.5 inches thick of a polyester-based polyurethane foam having a density of 7.5 pounds per cubic foot. The results obtained are presented in the following table.

TABLE VI

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase
300	47	5
164	114	5
47	~ 200	4

This Example further demonstrates the effectiveness of another grade of polyurethane foam.

polyester based polyurethane foam.**** Also, as noted in the following table, the Grand Isle crude oil in water dispersion was replaced with a dispersion of South Ponca Crude oil in water in the latter part of the run.

****This polyester-based polyurethane foam had a 10% maximum compression set, a 20 lbs/in.² minimum tensile strength, a 300% minimum elongation, and a 20% minimum resilience.

Example 8.

40 The run of Example 6 was repeated except that the bed of polyurethane foam employed therein was replaced with a bed 3.5 inches thick of 2.0 pounds per cubic foot

TABLE VII

Flow Rate, Barrel/Day/Ft. ² of Foam Surface	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase	
84	78	13.8	Grand Isle Crude
	222	10.6	
	130	15.3	
	120	6.7	
	120	14.2	
	112	7.6	
	120	8.4	
	133	10.3	
	188	17.2	
	242	14.4	
	349	15	S. Ponca Mississippi Chat Crude, API Gravity 43
300	132	11.2	
282	127	29	

5 This Example further demonstrates the use of flexible polyurethane foams for the coalescence of dispersions of oleophilic liquid in aqueous liquid. 10

Example 9.

The run of Example 2 was repeated except that the foam bed employed in Example 2 was replaced with a bed of polyester-based polyurethane foam having a commercial designation of Presto-Foam 945, having a depth of 4 inches and a density of 4.5 pounds per cubic foot. This foam was obtained from the Presto Manufacturing Company, Inc., 2 Franklin Avenue, Brooklyn, New York 11211. Data which were obtained are presented in the following table: 15

TABLE VIII

Flow Rate, Barrels/Day/Ft. ² of Foam Surface	Influent Oil Conc. (ppm) of Dispersion	Effluent Oil Conc. (ppm) of Aqueous Phase
111	486	10
112	387	14.6
112	472	15
113	240	23
112	195	15
112	267	16

This example demonstrates the process of the invention with yet another commercial polyurethane foam.

WHAT WE CLAIM IS:—

- 5 1. A process for separating the phases of a dispersion comprised of water and a liquid petroleum hydrocarbon wherein the process comprises passing the dispersion without previous coalescence through a coalescing material constituted by a layer of a permeable, flexible foam of polyurethane which has previously been saturated with liquid petroleum hydrocarbon, at a rate of flow sufficiently low to effect a coalescence of the dispersed phase, and at a pressure sufficient to substantially maintain the liquid petroleum hydrocarbon of the dispersion in the liquid state, permitting the thus coalesced dispersion to separate into a liquid petroleum hydrocarbon layer and a water layer, and withdrawing the separate layers.
- 10 2. A process as claimed in Claim 1 wherein the said rate of flow is 50 to 1000 barrels of the dispersion per square foot of the area of said foam layer per day; the permeable foam of polyurethane has a density of 0.8
- 15 20 25

to 7.5 pounds per cubic foot; and the operating temperature is 0° C to 100° C.

3. A process as claimed in Claim 1 or Claim 2 wherein the dispersion is a dispersion of a liquid petroleum hydrocarbon in water, wherein the liquid petroleum hydrocarbon dispersed phase comprises a trace to one part by weight of liquid petroleum hydrocarbon per 100 parts by weight of water, and wherein a flow rate of 50 to 1,000 barrels of dispersion per square foot of foam area per day is employed.

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4. A process as claimed in Claim 3, wherein the liquid petroleum hydrocarbon is a crude oil, wherein the dispersion contains 50 to 350 ppm of crude oil, and wherein the depth of the polyurethane foam layer is 3.5 to 12 inches.

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5. A process according to Claim 1, substantially as hereinbefore described.

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For the Applicants:—

F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
Lincoln's Inn Chambers,
40—43, Chancery Lane, London, W.C.2.